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(54) Title: ALKOXYLATED PHOSPHATE ESTERS USEFUL AS SECONDARY ADHESION PROMOTERS, INTERNAL MOLD RELEASE AGENTS AND VISCOSITY MODIFIERS

(57) Abstract: The present invention relates to the use of alkoxylated phosphate esters as internal mold release agents, secondary adhesion promoters and/or viscosity modifiers in polyester resin compositions, plastic parts comprising such resin compositions and methods of manufacturing said plastic parts. The alkoxylated phosphate esters disclosed herein are virtually free of acid and are capable of functioning as both internal mold release agents and viscosity modifiers in filled polyester resin systems. Additionally, the use of the alkoxylated phosphate esters in accordance with the instant invention provides for dramatically reduced corrosion of metal parts (e.g., a metal mold) which come in contact with the resin compositions during production of thermoset composites. The instant invention further relates to a process for preparing pultruded parts utilizing said alkoxylated phosphate esters. The alkoxylated phosphate esters generally display excellent viscosity reduction properties without the use of chlorinated solvents or styrene diluents associated with conventional polyester resin viscosity reducing agents.

ALKOXYLATED PHOSPHATE ESTERS USEFUL AS SECONDARY ADHESION PROMOTERS, INTERNAL MOLD RELEASE AGENTS AND VISCOSITY MODIFIERS

5

BACKGROUND OF THE INVENTION

10 **Field of the Invention**

The present invention relates to the use of alkoxylated phosphate esters as secondary adhesion promoters, internal mold release agents and/or viscosity modifiers in polyester resin compositions and methods of manufacturing plastic components using such esters. The invention further relates to alkoxylation as a means to neutralize acidic phosphate esters, whereby such alkoxylated phosphate esters aid in the production of thermoset composites, bulk molding compounds and sheet molding compounds. More specifically, the alkoxylated phosphate esters disclosed herein are virtually free of acid (i.e. phosphoric acid moieties) and are capable of functioning as internal mold release agents and/or viscosity modifiers in filled polyester resin systems. The use of the alkoxylated phosphate esters in accordance with the instant invention provides for increased secondary adhesion of a variety of materials to composites prepared from resin systems which contain such alkoxylated phosphate esters. Additionally, the use of the alkoxylated phosphate esters in accordance with the instant invention provides for dramatically reduced corrosion of metal parts (e.g., a metal mold) which come in contact with the resin compositions during production of plastic components. The instant invention further relates to a process for preparing plastic parts, including thermosetting composites, pultruded composites, bulk molding and sheet molding compounds, utilizing said alkoxylated phosphate esters. The alkoxylated phosphate esters described herein

generally display excellent viscosity reduction properties without the use of chlorinated solvents and/or allow for decreased usage levels of styrene diluents associated with conventional polyester resin viscosity reducing agents.

Description of Related Art

5 There are numerous compounds that are used in the production of plastic components. Often, the components are formed using a molding process. To successfully manufacture a molded plastic part, a mold release agent is used in the manufacturing process to permit release of the finished component from the mold.

One general class of mold release agent is "external" mold release agents.

10 External mold release agents are applied directly to the mold. This procedure increases the manufacturing time and must be repeated every one to five parts. In addition, the mold release agent builds up on the mold upon repeated application, so the mold must be cleaned periodically with a solvent or washing agent. Reapplication and cleaning are undesirably costly and time consuming. A second general class of mold release agent is
15 "internal" mold release agents. Internal mold release agents are added directly into the molding compound. Since they do not have to be continuously reapplied to the mold, internal mold release agents increase productivity and reduce cost.

There are many examples of compounds containing internal mold release agents for manufacturing various types of plastic components. U.S. Pat. Nos. 4,408,000 and
20 4,409,351 disclose the use of fatty acids in the production of thermoplastic parts, which generally are flexible.

Various mold release agents are used in the production of other flexible elastomers, such as polyurethanes and other foams. U.S. Pat. No. 4,753,966 discloses the use of a zinc salt dissolved in an amine liquid as a mold release agent in the

production of polyurethanes. Similarly, U.S. Pat. No. 5,182,034 discloses the use of a metal salt combined with an amine as a mold release agent in the production of polyurethanes.

U.S. Pat. No. 5,576,409 discloses the use of a fatty acid amide as a mold release agent. U.S. Pat. No. 4,551,507 discloses a molding compound including a linear saturated polyester. The mold release agent is a metallic amine carboxylate formed from a metal-containing salt.

One type of molding compound, not described in any of the above patents, is an unsaturated polyester thermosetting molding compound. Such compounds sometimes 10 are referred to as unsaturated polyester resin systems because they all include an unsaturated polyester resin. These compounds are well known in the art. For example, U.S. Pat. Nos. 5,585,439, 5,561,192, 5,449,549, 5,445,877, and 5,412,003 each describe various formulations of unsaturated polyester resin systems. They are used in the production of strong, rigid plastic components used as automotive parts, boat hulls, 15 general transportation products, appliances, furniture, computer components, electrical products--anywhere where it is desirable to have a strong, rigid, intricate plastic part manufactured to a stringent tolerance.

Two main types of unsaturated polyester thermosetting molding compounds are known as bulk molding compounds ("BMC") and sheet molding compounds ("SMC"). 20 Such compounds include an unsaturated polyester resin. These resins, with a catalyst, can be cured in a heated mold to form a clear, hard composition. As it cures, the resin has a tendency to shrink slightly, thereby aiding in the release from the mold. The resultant composition, however, is extremely brittle, and therefore not useful in most applications. Therefore, a reinforcement component is added. A filler component,

generally a fine ground mineral, is also added to improve appearance and surface characteristics. One common reinforcement material is chopped fiberglass. The resin, glass, and filler can be mixed directly to form a compound having a dough-like consistency, which is then added to a mold. Such a compound is commonly known as a
5 bulk molding compound or BMC. Alternatively, as is known in the art, the molding compound can be formed into a thin sheet, called a sheet molding compound or SMC. The SMC is then molded. U.S. Pat. No. 5,445,877, which is incorporated here by reference, provides an example of the making of a sheet molding compound. Both BMCs and SMCs are particularly useful in manufacturing strong, intricate components to
10 stringent tolerances. As, for example, in some of the systems described in the patents referenced above, other components commonly used in BMCs and SMCs include a low profile thermoplastic additive, a crosslinking monomer, and a thickener. Optionally, a pigment (or a dispersion thereof) can also be included to produce a colored molded part. The use of such additives in unsaturated polyester thermosetting molding compounds,
15 for both BMC and SMC processes, is well known in the art.

When mixed, the resin penetrates or wets the fiberglass reinforcement, thereby dispersing throughout the molding compound. It is desirable to have as much filler as possible in the BMC or SMC, since filler is far less expensive than resin. The addition of filler (and glass), however, inhibits the shrinking that occurs when the resin is molded by
20 itself. BMCs and SMCs, therefore, require that a mold release agent be added. The more filler added, the harder it is to release the finished component, and the more mold release agent that must be used. Likewise, the more intricate the part, the harder it is to release, and the more mold release agent that must be used as well.

The most common mold release agent used in BMC and SMC processes is zinc

stearate. It is estimated that zinc stearate is used as the mold release agent in as much as 90% of BMC and SMC processes. Zinc stearate acts by exuding to the surface of the molding compound, thereby contacting the mold and providing lubrication at the mold surface to permit release. Zinc stearate is a fine, dusty powder, which creates several difficulties. As a powder, zinc stearate is difficult to disperse in the liquid resin, and thus, lumps can form. When lumps of zinc stearate exude to the mold surface, the result is imperfections or pitting on the surface of the finished product. These imperfections interfere with the subsequent treatment of the surface of the part, including interference with the application of vapor deposited metals, laminants, adhesives, paints and the like commonly applied to the surface of molded plastic parts. Depending on the part and its use, the part must be sanded, specially washed, or otherwise treated before adding surface coatings. For example, Uddin, et al., "Laser Surface Engineering of Automotive Components", Plastics Engineering (1997), discloses a method by which SMC automotive parts are treated with a laser to improve surface characteristics. Sometimes, imperfect parts must be discarded. The problems encountered using zinc stearate become more acute as the component becomes more intricate, since more mold release agent must be used.

Powder mold release agents such as zinc stearate also reduce the amount of filler that can be used in that they raise the viscosity of the liquid polyester resins. As a result, powder mold release agents increase the viscosity of the molding compound inhibiting the wetting of the reinforcement by the resin. Thus, more resin and less filler must be used, which increases raw material costs. Zinc stearate use in SMC/BMC applications has the primary drawback of being a solid. The material must be dispersed in the resin system; insufficient dispersion can cause a concentration of zinc stearate at

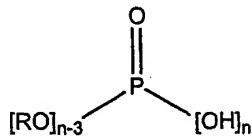
the surface of the resin mixture and hinder top coat adhesion during application. Such adhesion affects the coating of the part with such materials as inks, paints, and adhesives.

To overcome the drawbacks of powder mold release agents like zinc stearate,
5 there has been a need for a liquid mold release agent for use in BMC and SMC processes. State-of-the-art liquid mold release agents are liquid zinc salts and phosphate esters. These materials, however, do not provide sufficient mold release activity for use in the low-shrink resin systems of BMC and SMC processes, and particularly are unsuitable for use in the molding of intricate parts to stringent tolerances.
10 These materials also are very expensive. Thus, for the vast majority of BMC and SMC processes, powder mold release agents such as zinc stearate (and to a lesser extent calcium stearate) remain the primary currently available option. U.S. Pat. No. 5,883,166 discloses a method for neutralizing carboxylic acids with specialty amines to afford products that are liquid in nature. The products of this invention are liquid in nature and
15 provide an acid-free media from which to work from.

Two other types of processes for molding with unsaturated polyester thermosetting molding compounds are pultrusion and wet-mat molding processes. In pultrusion, the reinforcement, usually fiberglass, is wheeled off a spool, dipped into a resin mixture, and pulled through a heated die to cure the compound. A mold release agent is used as part of the resin mixture to release the compound from the die. In wet-
20 mat molding, a reinforcement mat is layed on the mold and the molding compound is poured on top of the mat. A mold release agent likewise is used in wet-mat processes. Pultrusion and wet-mat molding compounds differ from BMCs and SMCs partly in that no low profile thermoplastic additive or thickening agent is used. BMCs and SMCs are

preferred for more complex molded components, and generally are more difficult to release.

The use of phosphate esters as internal mold release agents is somewhat common in the fiber reinforced plastic industry. Typical resin formulations comprise a polyester or vinylester resin with the addition of styrene, filler (typically clay, calcium carbonate, or aluminum trihydrate), catalyst, and an internal mold release agent. The use of any particular mold release agent varies depending upon the final application. Pure phosphate esters, such as ZELEC® UN, a phosphate ester of the general formula:



with R being a C₈₋₁₆ alkyl group and n being 1 or 2, available from the Stepan Company, can also hinder many processes due to the high acid number inherent in such materials (for Zelec® UN, 270 mg KOH/g sample). As used herein and commonly understood by those skilled the art, acid number or OH value means "hydroxyl value", a quantitative measure of the concentration of hydroxyl groups or a quantitative measure of the concentration of acid groups, usually stated as mg KOH/g, i.e., the number of milligrams of potassium hydroxide equivalent to the hydroxyl or acid groups in 1g of substance.

In a typical pultrusion process, there is industry-wide concerned regarding the wear on the metal die due to the acidity of the release agent used. Also, the resin bath utilized in such processes can have a tendency to build viscosity over time as the acid interacts with fillers such as calcium carbonate and aluminum trihydrate. This increase in viscosity can cause a dramatic, undesirable decrease in fiber wet out, leading to

inferior final physical properties of the resin parts. Other applications have utilized pure phosphate esters as mold release agents; see, e.g., U.S. Pat. No. 5,962,561, issued Oct. 5, 1999, disclosing the use of phosphate esters as internal mold release agents for polyurethane and polythiourethane resin systems. Current neutralization techniques in 5 the industry utilize amines as the key component to the reduction in the release agent's acidity. Axel Plastics INT-PS125 and INT-PUL24 are exemplary "phosphate esters with a proprietary mixture of primary and secondary amines". (See MSDS for INT-PS125 and INT-PUL24 from Axel Plastics).

Other phosphate ester derivatives have been used to reduce the viscosity highly 10 filled polyester systems. U.S. Pat. No. 5,262,212 discloses the use of a phosphated polyester available from BYK Chemie as a means to reduce the viscosity of a highly filled polyester system. This product is disclosed as BYK W-995 and contains approximately 48% of the active phosphate polyester, about 25 % of naptha and light 15 aromatic solvents, about 25 % of 1-methoxy-2-propanol acetate, and about 2 % phosphoric acid. U.S. Pat. No. 5,380,776 discloses the use of C₄₋₁₈ alkyl, cycloalkyl, alkenyl, or alkynyl phosphates as viscosity reducers of polyester resin systems filled with an inert filler. Additionally, EP 0 342 815 discloses phosphate esters based on caprolactone polymers as viscosity reducers for filled polyester systems.

The synthesis of alkoxylated phosphophate esters is generally described in U.S. 20 Pat. No. 2,586,897 and in "Phosphorus and its Compounds" J.R. Van Wazer, ed, Vol II pp. 1227-1229 (Interscience Publishers Inc., New York, 1961), both incorporated herein by reference. The surfactant properties of such materials are generally described by Perka et al (Pollena: Tluszcze, Srodki Piorance, Kosmet, 1978, Vol 22, Number 11, 165-175).

Several alkoxylated phosphate esters have been used in fiber reinforced plastic systems (see e.g., U.S. Pat. No. 4,282,133), whereby such esters must be dissolved in a chlorinated solvent with the filler, mixed, dried down, then added to the polyester resin. In accordance with the instant invention, the alkoxylated phosphate esters are added 5 directly to the polyester resin with mixing; no addition of harmful chlorinated solvent and/or separate drying steps are needed.

The foregoing description of the related art indicates that a variety of mold release agents and/or viscosity modifiers are known, along with a variety of processes to utilize such materials to produce thermoset resins and various plastic parts. The 10 aforementioned mold release agents and/or viscosity modifiers have various end-use property limitations and/or undesirable processing limitations. Thus, a need exists for a superior processable internal mold release agent which is liquid at room temperature (i.e., about 25°C), can be readily prepared at low cost and is highly compatible with a variety of resin systems. There is a need for an internal mold release agent which 15 provides superior mold release properties during use, including during the formation of intricate plastic parts. There is also a strong need for an internal mold release agent which is free of acid (i.e., acid moieties in the mold release agent), lacks the presence of salts and/or reduces viscosity of the resin system during use. Additionally, there is a need for an internal mold release agent which not only provides superior mold release 20 properties during the manufacture of plastic parts, but also allows for sufficient secondary adhesion of a variety of materials to the finished plastic part, such as paints, dyes, glues, additional plastic parts, etc. Typically, mold release agents promote release from the mold, and thus inhibit often desirable secondary adhesion of the plastic part to other materials. Generally, the more mold release agent used, the more difficult it is to

obtain sufficient levels of secondary adhesion to the plastic part.

- It has been surprisingly discovered, that certain alkoxyated phosphate esters detailed herein are capable of functioning as mold release agents, secondary adhesion promoters and/or viscosity modifiers, which are both highly compatible with a variety of resin systems and eliminate many of the aforementioned disadvantages associated with conventional solid and/or liquid mold release agents. In addition to highly desirable mold release properties, the alkoxyated phosphate esters disclosed herein are essentially free of acid, eliminating the need for the use of amines or other salt forming materials for neutralization prior to or contemporaneous with their use.
- 10 The present invention provides internal mold release agents which are essentially 100 % active materials and also significantly reduce corrosion of metal dies used in the formation of various plastic parts, and significantly reduce the viscosity of filled resin systems. Very surprisingly, it has also been discovered that use of the alkoxyated phosphate esters detailed herein in the various resin systems not only provides for excellent mold release properties, but also improves secondary adhesion of a variety of materials to the plastic components produced from the resin systems.
- 15

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SUMMARY OF THE INVENTION

It is an object to the present invention to provide an improved polyester resin system comprising an alkoxylated phosphate ester as a mold release agent and/or viscosity reducing agent, methods of preparing such esters and systems and plastic components and methods of manufacturing such plastic components utilizing the resin systems detailed herein.

5 It is a further object of the present invention to provide improved internal mold release agents for use in polyester resin systems and particularly for use in BMC and SMC manufacturing processes. It is a further object of the present invention that said 10 mold release agents be a liquid at about 25°C and provide improved mold release activity and enhanced surface characteristics of the final product to permit the immediate application of various coatings, adhesives, or metals, and permit a higher proportion of filler to be used in the system, thereby increasing productivity, lowering cost, and improving the quality of the final product.

15 Another object of the invention is to provide alkoxylated phosphate esters for use in polyester resin systems, whereby the viscosity of such systems is significantly reduced by the inclusion of such esters. Another objection of the invention relates to polyester resin systems which incorporate alkoxylated phosphate esters as internal mold release agents and/or viscosity reducing agents, whereby the system is basically free of acid 20 moieties in the internal mold release agents and/or viscosity reducing agents, without the use of amines or other salt forming species for neutralization.

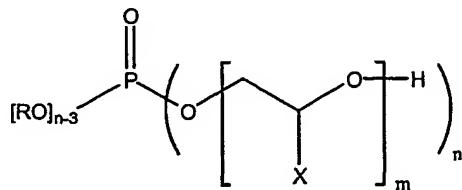
The invention relates to a method of reducing metal corrosion during the use of polyester resin systems and/or formation of plastic parts from such systems, comprising adding an effective amount of an alkoxylated phosphate ester as internal mold release

agents and/or viscosity reducing agents to such systems. Yet another embodiment of the instant invention relates to the use of alkoxylated phosphate esters to improve pigment disperment in various resin systems.

The invention further relates a method of increasing the secondary adhesion capacity of a plastic component, a thermosetting composite, a pultrusion based composite, bulk molding and/or sheet molding compounds which have been prepared from a resin system as detailed herein, comprising adding to the resin system an effective amount of an adhesion promoter which is an alkoxylated phosphate ester. Yet another embodiment of the instant invention relates to the use of alkoxylated phosphate esters to improve pigment disperment in various resin systems.

Accordingly, the present invention generally relates to a resin system suitable for preparing plastic components comprising:

- a) an unsaturated polyester resin;
- b) a crosslinking monomer;
- c) a filler; and
- d) an alkoxylated phosphate ester of the formula



wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and X is hydrogen or methyl. Somewhat preferably, each R is independently C₈₋₁₆ alkyl, n is 1 or 2, m is 1 and X is hydrogen. Also somewhat preferably, each R is independently C_{12-C₁₆} alkyl, n is 1 or 2, X is hydrogen, and m = 1 - 2. Optionally, the resin system can further comprising thickeners, low profile thermoplastic additives,

pigments and catalysts. Also, the resin system somewhat preferably has a ratio of (d) to (a) of from about 0.20 parts (d) : 100 parts (a) to about 10 parts (d): 100 parts (a). More preferably, the ratio of (d) to (a) is from about 0.20 parts (d) : 100 parts (a) to about 6 parts (d): 100 parts (a).

5 The resin systems of the present invention can be used to manufacture molded plastic components. Accordingly, the invention also generally relates to plastic parts, thermosetting composites, pultrusion based composites, BMC and/or SMC compounds which comprise the resin system and a reinforcement material such as chopped fiberglass, roving fiberglass, mat fiberglass, carbon fiber or combinations thereof.

10 The polyester resin, filler, reinforcement material, crosslinking monomer, liquid mold release agent, and the other additives are all mixed in bulk at room temperature in a manner known to those skilled in the art. Optionally, the resin system in combination with the reinforcement material can then be formed into a thin sheet. The bulk or sheet molding resin system is then placed into a mold, which is heated at a temperature and for a time sufficient to cure the compound. The product is then released from the mold and cooled. The resultant product is a strong, rigid plastic component having enhanced surface characteristics suitable for immediate treatment with vapor deposited metals, paints, adhesives, laminants, and the like.

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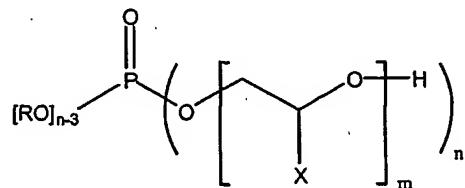
These and other objects and advantages are achieved by the detailed invention
20 description below.

DETAILED DESCRIPTION OF THE INVENTION

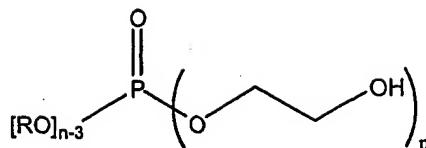
The resin systems of the present invention generally comprise an unsaturated polyester resin, a crosslinking monomer, a filler, a catalyst, and an alkoxylated phosphate ester as a mold release agent and/or viscosity reducer. The general inventive resin systems can be tailored to be suitable for the production of thermosetting composites, pultrusion based composites, bulk molding compounds and sheet molding compounds, with appropriate selection of reinforcement material.

Accordingly, the present invention relates to a resin system suitable for preparing thermosetting composites comprising:

- 10 a) about 100 phr of an unsaturated polyester resin;
- b) about 1 – 5 phr of a crosslinking monomer;
- c) about 10 – 300 phr of a filler; and
- d) about 0.5 – 5 phr of an alkoxylated phosphate ester of the formula



- 15 wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and each X is independently hydrogen or methyl. Somewhat preferably, each R is independently C₈₋₁₆ alkyl, n is 1 or 2, m is 1 - 2 and X is hydrogen. Also somewhat preferably, each R is independently C_{12-C₁₆} alkyl, n is 1 or 2, X is hydrogen, and m = 1 - 2. As used herein and commonly understood by those skilled the art, 'phr' means parts per hundred resin. In a highly preferred embodiment, the alkoxylated phosphate ester is of the formula

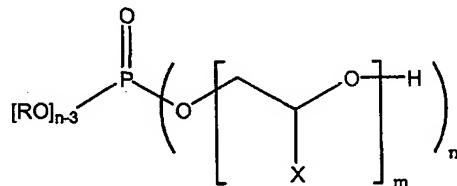


wherein each R is independently C₈₋₁₆ alkyl and n is 1 or 2. Optionally, the resin system of this embodiment can further comprising thickeners, low profile thermoplastic additives, pigments, catalysts.

5 Further with respect to thermosetting composites, the invention relates a thermosetting composite comprising:

a) a resin system comprising

- i) about 100 phr of an unsaturated polyester resin;
- ii) about 1 – 5 phr of a crosslinking monomer;
- 10 iii) about 10 – 300 phr of a filler; and
- iv) about 0.5 – 5 phr of an alkoxylated phosphate ester of the formula



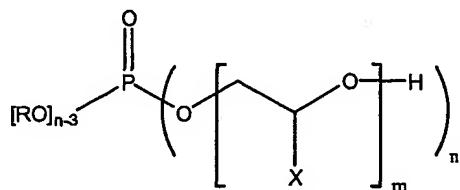
wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and X is hydrogen or methyl; and

15 b) a reinforcement material selected from the group consisting of chopped fiberglass, roving fiberglass, or mat fiberglass, carbon fiber or combinations thereof.

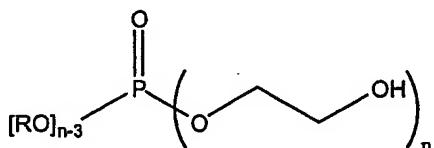
Somewhat preferably, the thermosetting composite comprises from about 20 – 70 % by weight of the reinforcement material, based on the total weight of the thermosetting composite. Optionally, the resin system of this embodiment can further comprising thickeners, low profile thermoplastic additives, pigments, catalysts.

The present invention further relates to a resin system suitable for preparing pultrusion based composites comprising:

- a) about 100 phr of an unsaturated polyester resin;
- b) about 1 – 5 phr of a crosslinking monomer;
- 5 c) about 20 – 200 phr of a filler; and
- d) about 0.5 – 3 phr of an alkoxylated phosphate ester of the formula



wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and each X is independently hydrogen or methyl. In accordance with this embodiment
10 and somewhat preferably, each R is C_{8-16} alkyl, n is 1 or 2, m is 1 - 2 and X is hydrogen. Also somewhat preferably, each R is independently C_{12-16} alkyl, n is 1 or 2, X is hydrogen, and m = 1 - 2. In a highly preferred embodiment, the alkoxylated phosphate ester is of the formula

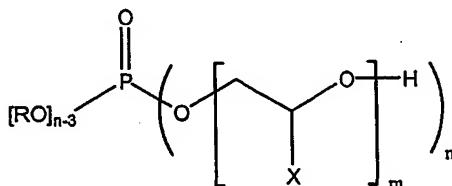


15 wherein each R is independently C_{8-16} alkyl and n is 1 or 2. Optionally, the resin system of this embodiment can further comprising thickeners, low profile thermoplastic additives, pigments and catalysts.

Further with respect to pultrusion based composites, the invention relates a pultrusion based composite comprising:

- 20 a) a resin system comprising

- i) about 100 phr of an unsaturated polyester resin;
- ii) about 1 – 5 phr of a crosslinking monomer;
- iii) about 20 – 200 phr of a filler; and
- iv) about 0.5 – 3 phr of an alkoxylated phosphate ester of the formula



wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and X is hydrogen or methyl; and

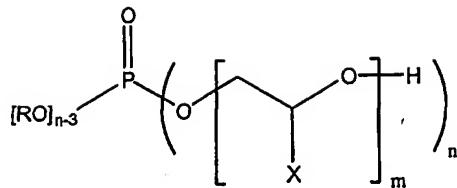
- b) a reinforcement material selected from the group consisting of chopped

fiberglass, roving fiberglass, or mat fiberglass, carbon fiber or combinations thereof.

- 10 Somewhat preferably, the thermosetting composite comprises from about 20 – 70 % by weight of the reinforcement material, based on the total weight of the thermosetting composite. Optionally, the resin system of this embodiment can further comprising thickeners, low profile thermoplastic additives, pigments, catalysts.

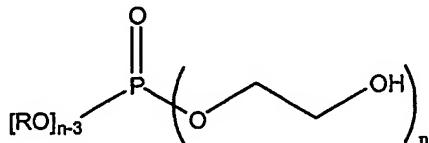
In another embodiment, the present invention relates to a resin system suitable 15 for preparing bulk molding compounds and/or sheet molding compounds comprising:

- a) about 100 phr of an unsaturated polyester resin;
- b) about 1 – 5 phr of a crosslinking monomer;
- c) about 100 – 300 phr of a filler; and
- d) about 0.5 – 5 phr of an alkoxylated phosphate ester of the formula



wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and each X is independently hydrogen or methyl. In accordance with this embodiment somewhat preferably, each R is C₈₋₁₆ alkyl, n is 1 or 2, m is 1 - 2 and X is hydrogen.

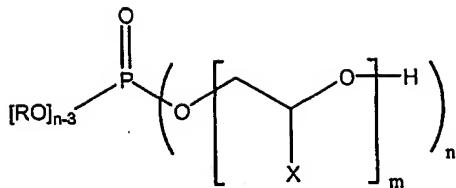
- 5 Also somewhat preferably, each R is independently C_{12-C₁₆} alkyl, n is 1 or 2, X is hydrogen, and m = 1 - 2. In a highly preferred embodiment, the alkoxyated phosphate ester is of the formula



wherein each R is independently C₈₋₁₆ alkyl and n is 1 or 2. Optionally, the resin system 10 of this embodiment can further comprising thickeners, low profile thermoplastic additives, pigments and catalysts.

Further with respect to bulk molding and sheet molding compounds, the invention relates a bulk molding and sheet molding compounds comprising:

- a) a resin system comprising
- 15 i) about 100 phr of an unsaturated polyester resin;
- ii) about 1 – 5 phr of a crosslinking monomer;
- iii) about 100 – 300 phr of a filler; and
- iv) about 0.5 – 5 phr of an alkoxyated phosphate ester of the formula

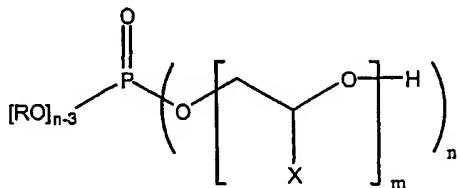


wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and X is hydrogen or methyl; and

- 5 b) a reinforcement material selected from the group consisting of chopped fiberglass, roving fiberglass, or mat fiberglass, carbon fiber or combinations thereof.

Somewhat preferably, the thermosetting composite comprises from about 20 – 70 % by weight of the reinforcement material, based on the total weight of the thermosetting composite. Optionally, the resin system of this embodiment can further comprising thickeners, low profile thermoplastic additives, pigments, catalysts.

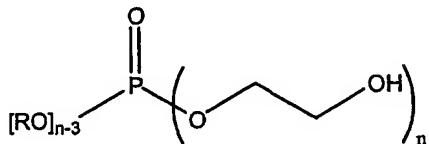
- 10 Also provided is a method of reducing the relative viscosity of a resin system suitable for preparing plastic components comprising adding to the resin system an effective amount of a viscosity reducing agent, the viscosity reducing agent being an alkoxylated phosphate ester of the formula



- 15 wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and X is hydrogen or methyl; and wherein the resin system comprises:

- a) an unsaturated polyester resin;
- b) a crosslinking monomer; and
- c) a filler.

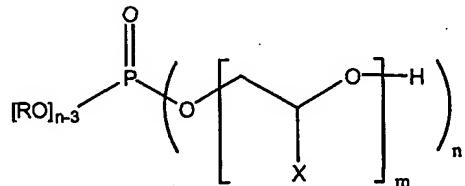
In accordance with this method somewhat preferably, each R is C₈₋₁₆ alkyl, n is 1 or 2, m is 1 - 2 and X is hydrogen. Also somewhat preferably, each R is independently C_{12-C₁₆} alkyl, n is 1 or 2, X is hydrogen, and m = 1 - 2. In a highly preferred method, the alkoxylated phosphate ester is of the formula



5

wherein each R is independently C₈₋₁₆ alkyl and n is 1 or 2. Optionally, the resin system of this embodiment can further comprising thickeners, low profile thermoplastic additives, pigments and catalysts.

A method is provided for increasing the secondary adhesion capacity of a plastic component which has been prepared from a resin system, comprising adding to the resin system an effective amount of an adhesion promoter which is an alkoxyated phosphate ester of the formula



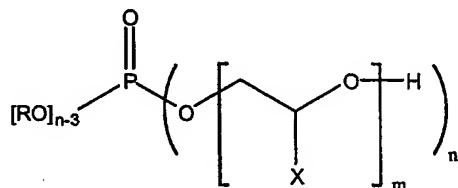
wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 - 10; and X is hydrogen or methyl; and wherein the resin system comprises:

- a) an unsaturated polyester resin;
- b) a crosslinking monomer; and
- c) a filler.

In accordance with this method, R is preferably C₈₋₁₆ alkyl, n is 1 to 2, X is hydrogen, and m = 1 - 2. In a somewhat preferred embodiment, R is preferably C_{12-C₁₆} alkyl, n is 1 or

2, X is hydrogen, and m = 1 - 2. Additionally, the resin system may further comprising a thickener, a low profile thermoplastic additive, a pigment or a dispersion of a pigment, a catalyst or a mixture of such materials. Somewhat preferably, the ratio of the adhesion promoter to (a) is from about 0.20 parts adhesion promoter : 100 parts (a) to about 10 parts adhesion promoter: 100 parts (a). In a highly preferred embodiment, the ratio of adhesion promoter to (a) is from about 0.20 parts adhesion promoter : 100 parts (a) to about 6 parts adhesion promoter: 100 parts (a).

5 A method is provided for increasing the secondary adhesion capacity of a thermosetting composite which has been prepared from a resin system, comprising adding to the resin system an effective amount of an adhesion promoter which is an 10 alkoxylated phosphate ester of the formula



wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 - 10; and X is hydrogen or methyl; and wherein the resin system comprises:

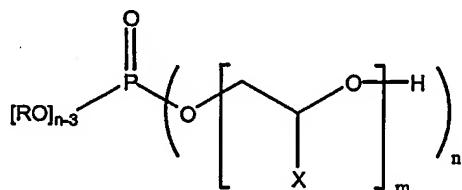
- 15 a) about 100 phr of an unsaturated polyester resin;
- b) about 1 - 5 phr of a crosslinking monomer; and
- c) about 10 - 300 phr of a filler.

In accordance with this method, R is preferably C₈₋₁₆ alkyl, n is 1 to 2, X is hydrogen, and m = 1 - 2. In a somewhat preferred embodiment, R is preferably C_{12-C16} alkyl, n is 1 or 20 2, X is hydrogen, and m = 1 - 2. Additionally, the resin system may further comprising a thickener, a low profile thermoplastic additive, a pigment or a dispersion of a pigment, a catalyst or a mixture of such materials. Additionally, the resin system may further

comprise a reinforcement material selected from the group consisting of chopped fiberglass, roving fiberglass, or mat fiberglass, carbon fiber or combinations thereof.

Preferably, the resin system will comprise from about 20 – 70 % by weight of the reinforcement material, based on the total weight of the thermosetting composite.

- 5 A method is provided for increasing the secondary adhesion capacity of a pultrusion based composite which has been prepared from a resin system, comprising adding to the resin system an effective amount of an adhesion promoter which is an alkoxylated phosphate ester of the formula



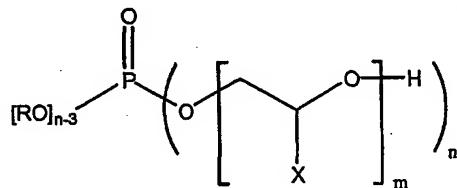
- 10 wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and X is hydrogen or methyl; and wherein the resin system comprises:
- about 100 phr of an unsaturated polyester resin;
 - about 1 – 5 phr of a crosslinking monomer; and
 - about 20 – 200 phr of a filler.

- 15 In accordance with this method, R is preferably C₈₋₁₆ alkyl, n is 1 to 2, X is hydrogen, and m = 1 - 2. In a somewhat preferred embodiment, R is preferably C_{12-C₁₆} alkyl, n is 1 or 2, X is hydrogen, and m = 1 - 2. Additionally, the resin system may further comprising a thickener, a low profile thermoplastic additive, a pigment or a dispersion of a pigment, a catalyst or a mixture of such materials. Additionally, the resin system may further
- 20 comprise a reinforcement material selected from the group consisting of chopped fiberglass, roving fiberglass, or mat fiberglass, carbon fiber or combinations thereof.

Preferably, the resin system will comprise from about 20 – 70 % by weight of the

reinforcement material, based on the total weight of the thermosetting composite.

A method is provided for increasing the secondary adhesion capacity of a bulk molding and sheet molding compound which has been prepared from a resin system, comprising adding to the resin system an effective amount of an adhesion promoter 5 which is an alkoxylated phosphate ester of the formula



wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and X is hydrogen or methyl; and wherein the resin system comprises:

- a) about 100 phr of an unsaturated polyester resin;
- 10 b) about 1 – 5 phr of a crosslinking monomer; and
- c) about 100 – 300 phr of a filler.

In accordance with this method, R is preferably C₈₋₁₆ alkyl, n is 1 to 2, X is hydrogen, and m = 1 - 2. In a somewhat preferred embodiment, R is preferably C_{12-C₁₆} alkyl, n is 1 or 2, X is hydrogen, and m = 1 - 2. Additionally, the resin system may further comprising a 15 thickener, a low profile thermoplastic additive, a pigment or a dispersion of a pigment, a catalyst or a mixture of such materials. Additionally, the resin system may further comprise a reinforcement material selected from the group consisting of chopped fiberglass, roving fiberglass, or mat fiberglass, carbon fiber or combinations thereof.

Preferably, the resin system will comprise from about 20 – 70 % by weight of the 20 reinforcement material, based on the total weight of the thermosetting composite.

Suitable catalysts useful in the various embodiments detailed herein include for example peroxides such as H₂O₂. Suitable thickeners include for example metallic

oxides such as magnesium oxide. The resin systems may also optionally include pigments, as are commonly used in the art. Additionally, in place of or in addition to the unsaturated polyester resin, the resin system may be based on vinyl ester resins, epoxy resins, phenoics resins, acrylic resins, or urethane based resins, or mixtures thereof.

Unsaturated polyester resins are well known in the art and are formed from the condensation reaction of a diol, such as ethylene glycol, propylene glycol, or dipropylene glycol, with a mixture of an unsaturated crosslinkable dicarboxylic acid or anhydride and a noncrosslinkable dicarboxylic acid or anhydride. Typically, mixtures of maleic anhydride and phthalic anhydride (or isophthalic acid) are used. The resins typically are diluted with crosslinking monomers such as styrene, alpha methyl styrene, vinyl toluene, or dialkyl phthalate.

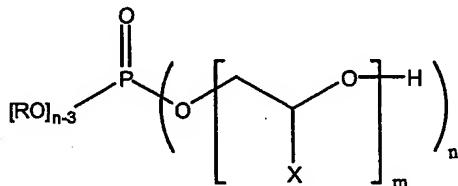
When unsaturated polyester resins crosslink they normally shrink. Low profile thermoplastic additives are incorporated to minimize the shrinking, which would otherwise lead to warpage and loss of dimensional tolerance in the molded part. A low profile thermoplastic additive particularly useable in the present invention is Neulon T Plus (a proprietary product from Union Carbide and it is based upon a polyvinyl acetate chemistry, it is a low profile additive that reduces the shrinkage properties of composites).

The filler generally is a fine ground mineral material. The preferred filler usable in the present invention is calcium carbonate. Other examples include clay and talc. Hydrated aluminum is commonly used in applications where flame retardance is important. When the filler is added to the resin, the resultant mixture has a dough-like consistency, which can then be molded. The filler improves the appearance and overall

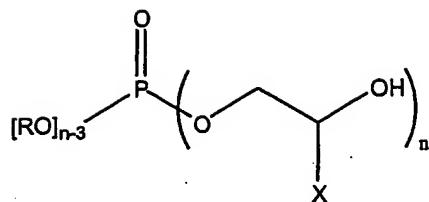
structure of the final product. As stated above, since filler is much cheaper than resin, it is desirable to use as high a proportion of filler as possible, while still having a sufficient amount of resin to disperse throughout the molding compound.

When preparing plastic components, a reinforcement material is generally added
5 to increase the strength of the final product. The preferred reinforcement material is fiberglass. In a BMC process, the fiberglass is chopped and added to the resin with the other components. In a SMC process, the resin and other components are mixed-and formed into a thin sheet. See, e.g., U.S. Pat. No. 5,445,877 referenced above. Other possible reinforcement materials include for example, cotton flock, cellulose flock, and
10 wood flower.

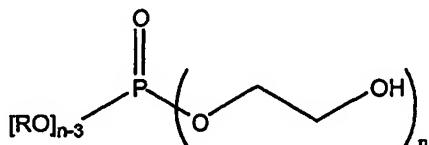
The internal mold release agent/viscosity reducing agent of the present invention is an alkoxylated phosphate ester of the general formula



wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 - 10;
15 and each X is independently hydrogen or methyl. Somewhat preferably, R is C₈₋₁₆ alkyl, n is 1 to 2, X is hydrogen, and m = 1 - 2. Also somewhat preferably, each R is independently C_{12-C16} alkyl, n is 1 or 2, X is hydrogen, and m = 1 - 2. Further in accordance with the various inventive embodiments, the alkoxylated phosphate ester is also somewhat preferably of the formula



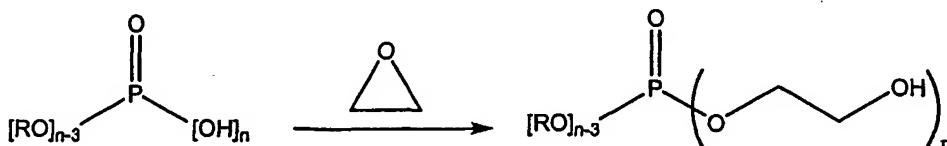
wherein each R is C₈₋₁₆ alkyl, n is 1 or 2, and each X is hydrogen or methyl. A highly preferred alkoxylated phosphate ester in accordance with each inventive embodiment is of the formula



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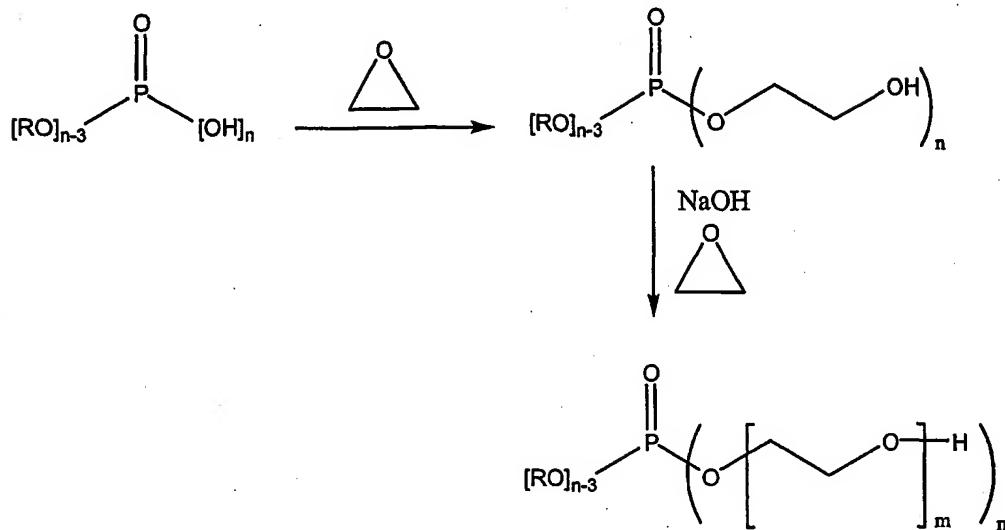
wherein each R is independently C₈₋₁₆ alkyl and n is 1 or 2.

The alkoxylated phosphate esters of the invention are generally prepared by the neutralization of a phosphoric acid ester with an alkoxylating agent. For example, a typical phosphoric acid ester such as Zelec® UN (available from Stepan Company) is neutralized with ethylene oxide to an acid value of <5 mg KOH/g from an original value 10 of 270 mg KOH/g sample, as shown by the following reaction scheme:



wherein R is C₈₋₁₆ alkyl and n = 1 – 2. This ethoxylated phosphate ester is soon to be available under the trade name ZELEC® LA-1 from Stepan Company, Northfield, Illinois. Also soon to be available, and highly useful in accordance with the various 15 embodiments of the instant invention, is ZELEC® LA-2, where R is C₁₂₋₁₆ alkyl and n = 1 – 2. It is anticipated that the desired number of moles of alkoxylating agent may be optionally added by use of standard base catalysis after the initial

alkoxylation/neutralization as shown by the follow reaction scheme:



wherein R is C₈₋₁₆ alkyl, n = 1 – 2 and m = 1 – 10.

One of the main advantages of the present invention is found in the fact that the internal mold release agent is a liquid at room temperature, i.e., 25°C. The phosphate ester and ethylene oxide are simply reacted in a manner well known in the art in the desired ratios; a specific production procedure is given in the experimental section below. Because they are liquids, the internal mold release agents of the present invention readily disperse in the liquid resin without forming lumps and often desirably significantly lower the resin systems viscosity.

All documents, e.g., patents and journal articles, cited above or below are hereby incorporated by reference in their entirety. In the following examples, all amounts are stated in percent by weight of active material unless indicated otherwise. One skilled in the art will recognize that modifications may be made in the present invention without deviating from the spirit or scope of the invention. The invention is illustrated further by the following examples which are not to be construed as limiting the invention or scope of the specific procedures or compositions described herein. All levels and ranges,

temperatures, results etc., used herein are approximations unless otherwise specified.

All viscosity data is reported in centipoises (cPs), unless otherwise noted.

The following examples exemplify the advantages of the alkoxylated phosphate esters in polyester resin systems for viscosity reduction, as internal mold release agents, 5 as styrene suppression agents, and for reduced corrosion of metal based on reduced acidity. The definitions and CTFA designations used in the present invention are generally shown below:

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15

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| <u>Component</u> | <u>Supplier</u> | <u>Function</u> | <u>Description</u> |
|--------------------------|--------------------------|---|---|
| Polyester Resin P-706 | AOC International | Resin | Polyester resin |
| ASP-400 Clay | Englehardt Corporation | Filler | Aluminum Silicate |
| Stryene | Various Suppliers | Diluent, Solvent Crosslinker | Styrene (Lab Material J.T. Baker) |
| Perkadox 16 | Akzo Nobel Chemicals Inc | Low Temperature Catalysts | Di-(4-tert-butylcyclohexyl) peroxydicarbonate |
| Esperox 10 | Witco Corporation | High Temperature Catalysts | Tert-Butyl Peroxybenzoate |
| Zelec® UN* | Stepan Company | Acidic Precursor Material | C8-16 Phosphoric Acid Ester |
| Zelec® LA-1* | Stepan Company | Viscosity Modifier/ Mold Release Agent | Alkoxylated C8-16 Phosphoric Acid Ester |
| Zelec® LA-2* | Stepan Company | Viscosity Modifier/ Mold Release Agent | Alkoxylated C12-16 Phosphoric Acid Ester |
| Camel Wite (3 micron) | Ecc International | Filler | Calcium Carbonate |

| HYMOD HYFLEX | J.M. Huber Corporation | Filler | Alumina Trihydroxide (non-fibrous) |
|-------------------------|------------------------|----------------------|---|
| SB-432 | J.M. Huber Corporation | Filler | Surface Modified Aluminium Trihydroxide |
| CM-2005Black Dispersion | Plasticolors | Dye for colored part | Carbon Black Pigment Dispersion |
| Polyester Resin 31022 | Reichhold | Resin | Polyester resin |
| Techlube CP-250 | Technick Products | Mold Release Agent | Partially neutralized phosphate ester |
| Moldwiz INT PUL-14 | Axel | Mold Release Agent | Partially neutralized phosphate ester |

*ZELEC is a registered trademark of Stepan Company, Northfield, Illinois

Example 1: Preparation of Alkoxylated Phosphate Ester Zelec LA-1

Zelec® UN (15.0 kg) was charged to a 5 gallon pressure reactor and heated to 90°C. Ethylene oxide (5.3 kg) was added with agitation incrementally to control 5 temperature (100°C max.) and pressure increases. Upon complete addition of ethylene oxide, the reaction temperature was held at 95°C for two hours. The acid value of the material was determined to be 3.43 by phenolphthalein pink endpoint. The final product was then vacuum stripped for 5.5 hours (70SCFM N₂ sweep; 28" Hg; 90°C), to give a material with a final acid value of 3.14.

10

Examples 2 – 5: Viscosity Reduction

Examples 2 – 6 show the viscosity reduction associated with an inventive internal mold release agent. These materials were by adding the alkoxylated phosphate ester from Example 1 to the resin with agitation, followed by the addition of styrene. Next, the 15 fillers and optional additives are added with continued agitation. The catalysts are typically mixed together with the free styrene and added to the system with the styrene. The final mixture is blended to achieve substantial homogeneity. The samples are then measured for viscosity on a Brookfield Viscometer at 12 rpm spindle speed and 30°C constant temperature.

20

Example 2: Clay-filled Viscosity Reduction

| <u>Component</u> | <u>Parts Per Hundred (phr)</u> |
|----------------------|--------------------------------|
| Polyester Resin P706 | 100 |
| ASP-400 Clay | 20 |
| Styrene | 1 |
| Perkadox 16 | 0.25 |
| Additives* | 0-1.5 |
| Esperox 10 | 0.50 |

*Additives may include those described herein, for example various pigments.

| | <u>Viscosity Additive</u> | <u>phr</u> | <u>Viscosity @ 1 hr.</u> | <u>Viscosity @ 3 hrs.</u> |
|---|---------------------------|------------|--------------------------|---------------------------|
| 5 | None | 0.0 | 3700 | 3800 |
| | ZELEC® UN | 1.0 | 4200 | 4400 |
| | ZELEC® LA-1 | 1.5 | 2600 | 2700 |

Example 3: Calcium Carbonate Filled Systems Viscosity Reduction

| | <u>Component</u> | <u>Parts Per Hundred (phr)</u> |
|----|----------------------|--------------------------------|
| 10 | Polyester Resin P706 | 100 |
| | Camel Wite 3 micron | 60 |
| | Styrene | 1 |
| | Perkadox 16 | 0.25 |
| | Additives* | 0-1.5 |
| 15 | Esperox 10 | 0.50 |

*Additives may include those described herein, for example various pigments.

| | <u>Viscosity Additive</u> | <u>phr</u> | <u>Viscosity @ 1 hr.</u> | <u>Viscosity @ 3 hrs.</u> |
|----|---------------------------|------------|--------------------------|---------------------------|
| 20 | None | 0.0 | 6291 | 5833 |
| | ZELEC® UN | 1.0 | 17705 | 17122 |
| | ZELEC® LA-1 | 1.5 | 5333 | 5333 |
| | ZELEC® MR-1 | 1.5 | 13814 | 13464 |

Example 4: Aluminum Trihydrate Filled Systems Viscosity Reduction

| | <u>Component</u> | <u>Parts Per Hundred (phr)</u> |
|----|----------------------|--------------------------------|
| 30 | Polyester Resin P706 | 100 |
| | SB-432 | 100 |
| | Styrene | 1 |
| | Perkadox 16 | 0.25 |
| | Additive* | 0-1.5 |
| | Esperox 10 | 0.5 |

*Additives may include those described herein, for example various pigments.

| | <u>Viscosity Additive</u> | <u>phr</u> | <u>Viscosity @ 1 hr.</u> | <u>Viscosity @ 3 hrs.</u> |
|----|---------------------------|------------|--------------------------|---------------------------|
| 35 | None | 0.0 | 16750 | 15583 |
| | ZELEC® UN | 1.0 | 29083 | 28116 |
| 40 | ZELEC® LA-1 | 1.5 | 14000 | 13500 |

Example 5: Aluminum Trihydrate Filled Systems Viscosity Reduction

| | <u>Component</u> | <u>Parts Per Hundred (phr)</u> |
|--|----------------------|--------------------------------|
| | Polyester Resin P706 | 100 |

| | | |
|---|--------------|-------|
| | HYMOD HYFLEX | 100 |
| | Styrene | 1 |
| | Perkadox 16 | 0.25 |
| | Additive* | 0-1.5 |
| 5 | Esperox 10 | 0.5 |

*Additives may include those described herein, for example various pigments.

| | <u>Viscosity Additive</u> | <u>phr</u> | <u>Viscosity @ 1 hr.</u> | <u>Viscosity @ 3 hrs.</u> |
|----|---------------------------|------------|--------------------------|---------------------------|
| 10 | None | 0.0 | 12021 | 12000 |
| | ZELEC® UN | 1.0 | 21000 | 21250 |
| | ZELEC® LA-1 | 1.5 | 14250 | 13917 |

Example 6: Calcium Carbonate Filled Systems with Black Pigment Dispersions

| | <u>Component</u> | <u>Parts Per Hundred (phr)</u> |
|----|----------------------|--------------------------------|
| | Polyester Resin P706 | 100 |
| | Camel Wite 3 micron | 60 |
| | Styrene | 5 |
| | Perkadox 16 | 0.25 |
| 20 | Additive* | 0-1.5 |
| | Esperox 10 | 0.50 |
| | Carbon Black | 5.0 |

*Additives may include those described herein, for example various pigments.

| | <u>Additive</u> | <u>phr</u> | <u>Viscosity @ 1 hr.</u> | <u>Viscosity @ 3 hrs.</u> |
|----|-----------------|------------|--------------------------|---------------------------|
| 25 | None | 0.0 | 1208 | 1208 |
| | ZELEC® UN | 1.0 | 12687 | 13166 |
| | ZELEC® LA-1 | 1.5 | 3604 | 3604 |

30

As is readily observed by Examples 2 -5 above, alkoxylated phosphate esters such as ZELEC® LA-1 and ZELEC® MR-1 provide improved viscosity reduction in the resin systems, as compared to no additive usage of a phosphoric acid ester such as ZELEC® UN.

35

Internal Mold Release

Examples 7-10 show the utility of the alkoxylated phosphate esters as internal

mold release agents by running on the following resin systems on an industrial pultrusion machine. All plastic parts produced were fiberglass reinforced plastic slats produced on a standard pultrusion machine, using a chromed steel mold. Pultrusion is a well known manufacturing process for producing continuous lengths of reinforced plastic structural shapes with constant cross-sections. Raw materials used in the process typically comprise a liquid resin mixture (containing resin, fillers and specialized additives) and flexible textile reinforcing fibers. As known to one of ordinary skill in the art, the process generally involves pulling the raw materials (rather than pushing, as is the case in extrusion) through a heated steel forming die using a continuous pulling device. The reinforcement materials are in continuous forms such as rolls of fiberglass mat and doffs of fiberglass roving. As the reinforcements are saturated with the resin mixture ("wet-out") in the resin bath and pulled through the die, the gelation, or hardening, of the resin is initiated by the heat from the die and a rigid, cured profile is formed that corresponds to the shape of the die. As commonly used in the pultrusion industry, "pull load" means or is a measure of force detected hydraulically by the pulling mechanism while pulling the composite through the dye. Pull loads for the inventive composition detailed below were determined to accurately measure mold release properties. As commonly used in the pultrusion industry, "flexural strength" means or is a measure of failure of a composite under flexural stress. It is tested in accordance with ASTM Method D-790. The flexural strengths of the inventive compositions detailed below were determined to ensure no detrimental effects on the final product were present due to the inclusion of the alkoxylated phosphate ester material.

Example 7: Clay-filled System

| <u>Component</u> | <u>Parts Per Hundred (phr)</u> |
|-----------------------|--------------------------------|
| Polyester Resin 31022 | 100 |
| ASP-400 Clay | 40 |

| | |
|-------------|-------|
| Styrene | 1 |
| Perkadox 16 | 0.25 |
| Additive* | 1-1.5 |
| Esperox 10 | 0.50 |

5 *Additives may include those described herein, for example various pigments.

| Additive | phr | Viscosity* | Pull Load | Flexural Strength** |
|-------------|-----|------------|-----------|---------------------|
| ZELEC® UN | 1.0 | 1770 | 766 lbs | 69.5 |
| ZELEC® LA-1 | 1.5 | 1500 | 825 lbs | 74.8 |

10

*Measured on the final composite part, in kpsi.

** Viscosity run at 30°C, Brookfield #27 Spindle, 12rpm.

Example 8: Calcium Carbonate Filled Systems

| 15 | <u>Component</u> | <u>Parts Per Hundred (phr)</u> | | |
|----|-----------------------|--------------------------------|--|--|
| | Polyester Resin 31022 | 100 | | |
| | Camel Wite 3 micron | 60 | | |
| | Styrene | 1 | | |
| | Perkadox 16 | 0.25 | | |
| 20 | Additive* | 1-1.5 | | |
| | Esperox 10 | 0.50 | | |

*Additives may include those described herein, for example various pigments.

| 25 | <u>Additive</u> | <u>phr</u> | <u>Visc*</u> | <u>Pull Load</u> | <u>Flexural Strength**</u> |
|----|-----------------|------------|--------------|------------------|----------------------------|
| | ZELEC® UN | 1.0 | 2895 | 100 lbs | 73.4 |
| | ZELEC® LA-1 | 1.5 | 1041 | 600 lbs | 75.0 |
| | ZELEC® LA-2 | 1.5 | 1100 | 250 lbs | 71.6 |
| | ZELEC® LA-1 | 2.5 | 1100 | 200 lbs | 73.3 |

30

*Measured on the final composite part, in kpsi

** Viscosity run at 30°C, Brookfield #27 Spindle, 12rpm.

Example 9: Higher CaCO₃ filled systems

35 This example is similar to Example 7, except that the CaCO₃ was increased to 80 parts with the ethoxylated UN to show the utility of increasing the filler content:

| <u>Additive</u> | <u>phr</u> | <u>Visc*</u> | <u>Pull Load</u> | <u>Flexural Strength**</u> |
|-----------------|------------|--------------|------------------|----------------------------|
| ZELEC® LA-1 | 1.5 | 1333 | 1784 lbs | 75.8 |

40 *Measured on the final composite part, in kpsi

** Viscosity run at 30°C, Brookfield # 27 Spindle, 12rpm.

Example 10: Aluminum Trihydrate Filled Systems

| Component | Parts Per Hundred (phr) |
|-----------------------|-------------------------|
| Polyester Resin 31022 | 100 |
| ATH – Treated | 100 |
| Styrene | 1 |
| Perkadox 16 | 0.25 |
| Additive* | 1-1.5 |
| Esperox 10 | 0.50 |

*Additives may include those described herein, for example various pigments.

| Additive | phr | Visc* | Pull Load | Flexural Strength** |
|-----------------|-----|-------|-----------|---------------------|
| ZELEC® LA-1 | 1.5 | 1854 | 2450 lbs | 76.0 |
| Techlube CP-250 | 1.5 | 2125 | 2386 lbs | 80.0 |

*Measured on the final composite part, in kpsi

** Viscosity run at 30°C, Brookfield #27 Spindle, 12rpm.

It should be noted, as with any of the above Examples 7 – 10, the styrene may be removed from the formulation to achieve the original viscosity of the system without the viscosity reducing additive.

Example 11: Corrosion Studies with ZELEC® UN, ZELEC® LA-1, and a partially neutralized phosphate ester, Moldwiz INT PUL-14.

Various mold release agents with various acid values were tested for corrosion studies. The method generally followed for corrosion testing is a modified version of ASTM G-30-72 "Standard Practice for Laboratory Immersion Corrosion Testing of Metals", incorporated in its entirety by reference. The method was modified in that 1) glass vials were used in place of flasks as the test apparatus; 2) the temperature of interest was 250°F; 3) no agitation of the liquid was performed. Double notched tool metal and double notched chrome plated tool metal were tested for 1 week at 250°F in

the various mold release solutions and observed for both visual changes and changes in weight due to corrosion.

Specifically, new coupons from Metal Testing Corporation were initially cleaned with soap and water and dried with acetone; a metal samples were handled with gloves to minimize any oils or dirt being deposited on the clean surfaces. Coupons were weighed and submerged ¾ of the length in the mold release agent. The vials containing the coupons/mold release agent were placed in a 250F oven for 48 hours. After this period of time the vials were removed and allowed to cool to about 25C. The coupons were removed from the mold release solution and cleaned again using soap and water, followed by acetone drying. The coupons were reweighed then placed back into the solution in the vial. The vials were then placed back into the oven for an additional 24 hours at 250F. After this period of time the vials were removed and allowed to cool to about 25C. The coupons were removed from the mold release solution and cleaned again using soap and water, followed by acetone drying. The coupons were finally weighed and the corrosion was measured as the amount of weight loss of the metal based on following formula:

$$(\text{final coupon weight}/\text{initial coupon weight}) \times 100 = \% \text{ weight loss}$$

Subjective visual evaluations of the coupons were also performed as indicated below.

| <u>Mold Release Agent</u> | <u>Acid Value*</u> | <u>1 wk. Visual</u> | <u>1 wk. % wt. loss (steel)</u> |
|---------------------------|--------------------|---------------------|---------------------------------|
| ZELEC® UN | 270 | Corroded Metal | 0.35% |
| Axel's Moldwiz INT-PUL 14 | 182 | Sl. Discoloration | 0.06% |
| ZELEC® LA-1 | 2 | No visual corrosion | 0.05% |

* Acid Value is in mg KOH/g sample

Thus, as shown in the test results, the use of the alkoxylated phosphate ester liquid mold release agents of the present invention provide numerous advantages over mold release agents currently used in unsaturated polyester resin compositions. The 5 present invention, therefore, is more successful in manufacturing intricate components to high tolerances. The superior mold release activity also permits a higher proportion of filler to be used as opposed to resin. In addition, unlike powder mold release agents, the liquid mold release agents of the present invention do not create lumps or other imperfections at the mold surface. Thus, products made according to the present 10 invention are immediately suitable for the application of vapor deposited metals, adhesives, laminants, paints, and similar coatings. The mold release agents also generally reduce the resin viscosity, and thus aid in the dispersion of the resin throughout the resin system compositions. This also permits a higher proportion of filler to be used. These advantages allow for a higher quality product at lower cost and 15 production time than is presently attainable.

Alternatively, although less preferred, the liquid mold release agents of the present invention can be used in combination with zinc or calcium stearate, liquid zinc salts, phosphate esters, or other mold release agents currently in use to improve their performance.

The liquid mold release agents of the present invention also can be used in 20 pultrusion and wet-mat molding processes, described above. In such processes, the resin compositions low profile thermoplastic additives and thickener are generally absent.

Example 12: Secondary Adhesion Studies with ZELEC® UN, ZELEC® LA-1, ZELEC LA-2 and a partially neutralized phosphosphate ester, Techlube CP-250.

5

The need for secondary adhesion is vitally important throughout the composite industry. Composites are a class of products that are used in a variety of ways. Many of these uses require that the composite be painted, dyed, joined to other pieces by gluing or other processes that require adhesion. Two different ASTM Methods were 10 utilized to evaluate the secondary adhesion characteristics of pultruded materials prepared in accordance with Example 8. The results of the various test performed are shown in Table 1 and Table 2 below.

The first test method was ASTM D-3359-95A, Standard Test Methods for Measuring Adhesion by Tape Test, incorporated herein in its entirety. This method 15 has two separate sections; section B used in evaluating the formulations. Section B, is a method that incorporates cross hatch criss cross cutting and generally allows for a more definitive number or scale. The panels were water rinsed, dried and then painted. The paint used is a two component polyurethane coating system by Sherwin Williams POLANE T and POLANE Reducer.

20 The second test method, which is used to determine adhesion of a glued FRP composite is ASTM Method D-5868-95 titled "Lap Shear Adhesion for Fiber Reinforced Plastic (FRP) Bonding", incorporated herein in its entirety. This method incorporates a process that involves the gluing of two separate composite sections together and then measuring the amount of force required to pull them apart. The 25 adhesive used was a structural adhesive from Ashland Specialty Chemical Company, PLIORGRIP 7770/100, a two component epoxy adhesive with a working time of 50

minutes. The only deviation from the prescribed ASTM Method was in the pretreatment step. This step is ASTM D-2093. D-2093 "Standard Practice for Preparation of Surfaces of Plastics Prior to Adhesive Bonding", incorporated herein in its entirety, calls for a sanding step to remove the glossy finish and all traces of dirt, grease, mold release, or other contaminants from the bonding surface. If this method is followed all traces of the mold release products will be removed and removes the effects of mold release on bonding. Instead of sanding, the panels were just water washed. This allowed for a more representative evaluation of the effect of the mold release agent on adhesion properties.

10 Typically, the more mold release agent which is added to a resin system, the worse adhesion of another material to the finished plastic part will be. Conceptually, this is true because standard mold release agents, by their very nature, are found on the surface of the finished plastic part and thus promote release of the plastic part from a mold, i.e., they prevent the part from sticking to the mold.

15 As can be seen in Table 1, when varying the mold release agent from ZELEC® UN to ZELEC® LA-1, minimal improvement is observed for lap shear properties. However, it is surprisingly seen that significantly increasing the amount of ZELEC® LA-1 greatly improves the lap shear properties of the material. As can be seen in Table 2, much more paint adheres to samples prepared with ZELEC® LA-1 or
20 ZELEC® LA-2, as compared to ZELEC® UN. A dramatic increase in paint adhesion is observed when an additional amount of ZELEC® LA-1 is added. Ordinarily, as with traditional mold release agents, one of ordinary skill in the art would not expect to observe such lap shear and/or adhesion properties when using such high levels of mold release agent.

Table 1: Lap Shear Test Results

| LAP SHEAR | | | | | |
|--------------|-----------------|-----------|-------------------|--------------|------------------|
| Water Washed | | | | | |
| Sample ID | MRA | MRA Level | Filler | Filler Level | Pull Force (lbs) |
| | | | | | |
| A | ZELEC® LA-2 | 1.5 pHr | CaCO ₃ | 60 pHr | 2811 |
| B | ZELEC® UN | 1.0 pHr | CaCO ₃ | 60 pHr | 1383 |
| C | ZELEC® LA-1 | 1.5 pHr | CaCO ₃ | 60 pHr | 1571 |
| D | TECHLUBE CP-250 | 1.5 pHr | CaCO ₃ | 60 pHr | 4153 |
| E | ZELEC® LA-1 | 2.5 pHr | CaCO ₃ | 60 pHr | 4281 |

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Table 2: Paint Adhesion Test Results

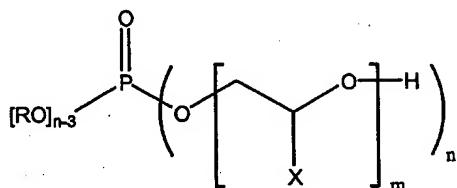
| Paint Adhesion | | | | | | |
|----------------|-------------|-----------|-------------------|--------------|----------|-----------|
| Water Washed | | | | | | |
| Sample ID | MRA | MRA Level | Filler | Filler Level | %Removed | %Adheared |
| E | ZELEC® LA-2 | 1.5 pHr | CaCO ₃ | 60 pHr | 32 | 68 |
| F | ZELEC® UN | 1.0 pHr | CaCO ₃ | 60 pHr | 97 | 3 |

| | | | | | | |
|---|-------------|---------|-------------------|--------|----|----|
| G | ZELEC® LA-1 | 1.5 pHr | CaCO ₃ | 60 pHr | 21 | 79 |
| H | TECHLUBE | 1.5 pHr | CaCO ₃ | 60 pHr | 0 | 10 |
| | CP-250 | | | | | 0 |
| I | ZELEC® LA-1 | 2.5 pHr | CaCO ₃ | 60 pHr | 0 | 10 |
| | | | | | | 0 |

The invention and the manner and process of making and using it, are now described in such full, clear, concise and exact terms as to enable any person skilled in the art to which it pertains, to make and use the same. It is to be understood that the foregoing describes preferred embodiments of the present invention and that modifications may be made therein without departing from the spirit or scope of the present invention as set forth in the claims.

WHAT IS CLAIMED IS:

1. A resin system suitable for preparing plastic components comprising:
 - a) an unsaturated polyester resin;
 - b) a crosslinking monomer;
 - c) a filler; and
 - d) an alkoxylated phosphate ester of the formula



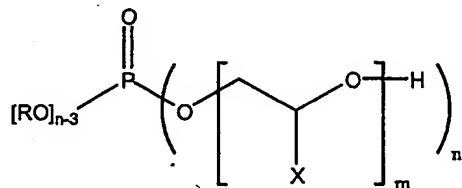
wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10;
and X is hydrogen or methyl.

2. The resin system according to claim 1, wherein R is C₈₋₁₆ alkyl, n is 1 to 2, X is hydrogen, and m = 1 – 2.
3. The resin system according to claim 2, further comprising a thickener.
4. The resin system according to claim 3, further comprising a low profile thermoplastic additive.
5. The resin system according to claim 4, further comprising a pigment or a dispersion of a pigment.
6. The resin system according to claim 1, further comprising a catalyst.

7. The resin system according to claim 1, wherein the ratio of (d) to (a) is from about 0.20 parts (d) : 100 parts (a) to about 10 parts (d): 100 parts (a).
8. The resin system according to claim 7, wherein the ratio of (e) to (a) is from about 0.20 parts (d) : 100 parts (a) to about 6 parts (d): 100 parts (a).

5 9. A plastic component comprising:

- a) a resin system comprising
- i) an unsaturated polyester resin;
 - 10 ii) a crosslinking monomer;
 - iii) a filler; and
 - iv) an alkoxylated phosphate ester of the formula



wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or

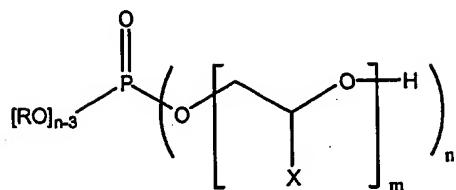
15 2; m = 1 – 10; and X is hydrogen or methyl; and

- b) a reinforcement material selected from the group consisting of chopped fiberglass, roving fiberglass, mat fiberglass, carbon fiber or a combination thereof;

10. A resin system suitable for preparing thermosetting composites comprising:

- 20 a) about 100 phr of an unsaturated polyester resin;
- b) about 1 – 5 phr of a crosslinking monomer;
- c) about 10 – 300 phr of a filler; and

d) about 0.5 – 5 phr of an alkoxyated phosphate ester of the formula



wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and X is hydrogen or methyl.

5

11. The resin system according to claim 10, wherein R is C₈₋₁₆ alkyl, n is 1 to 2, X is hydrogen, and m = 1 - 2.

10

12. The resin system according to claim 11, further comprising a thickener.

13. The resin system according to claim 12, further comprising a low profile thermoplastic additive.

14. The resin system according to claim 13, further comprising a pigment or a

15 dispersion of a pigment.

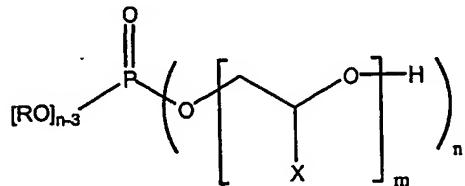
16. The resin system according to claim 14, further comprising a catalyst.

17. A thermosetting composite comprising:

20 a) a resin system comprising

- i) about 100 phr of an unsaturated polyester resin;
- ii) about 1 – 5 phr of a crosslinking monomer;

- iii) about 10 – 300 phr of a filler; and
- iv) about 0.5 – 5 phr of an alkoxylated phosphate ester of the formula



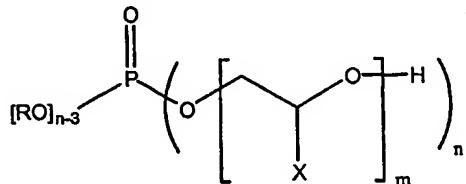
wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 5
2; m = 1 – 10; and X is hydrogen or methyl; and

- b) a reinforcement material selected from the group consisting of chopped fiberglass, roving fiberglass, or mat fiberglass, carbon fiber or combinations thereof.

10 17. A thermosetting composite according to claim 16, comprising from about 20 – 70 % by weight of the reinforcement material, based on the total weight of the thermosetting composite.

15 18. A resin system suitable for preparing pultrusion based composites comprising:

- a) about 100 phr of an unsaturated polyester resin;
- b) about 1 – 5 phr of a crosslinking monomer;
- c) about 20 – 200 phr of a filler; and
- d) about 0.5 – 3 phr of an alkoxylated phosphate ester of the formula



wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and X is hydrogen or methyl.

19. The resin system according to claim 18, wherein R is C₈₋₁₆ alkyl, n is 1 to 2, X is
5 hydrogen, and m = 1 - 2.

20. The resin system according to claim 19, further comprising a thickener.

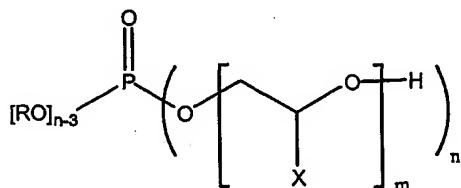
21. The resin system according to claim 20, further comprising a low profile
thermoplastic additive.

10 22. The resin system according to claim 21, further comprising a pigment or a
dispersion of a pigment.

23. The resin system according to claim 22, further comprising a catalyst.

15 24. A pultrusion based composite comprising:
a) a resin system comprising:

- a) a resin system comprising:
 - i) about 100 phr of an unsaturated polyester resin;
 - ii) about 1 – 5 phr of a crosslinking monomer;
 - iii) about 20 – 200 phr of a filler; and
 - iv) about 0.5 – 3 phr of an alkoxylated phosphate ester of the formula



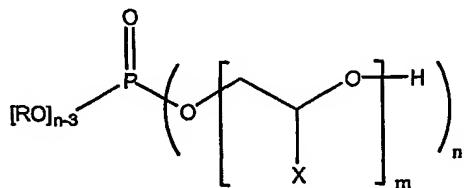
wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and X is hydrogen or methyl; and

- b) a reinforcement material selected from the group consisting of chopped fiberglass, roving fiberglass, mat fiberglass, carbon fiber or combinations thereof.

5

25. A pultrusion based composite according to claim 24, comprising from about 20 – 70 % by weight of the reinforcement material, based on the total weight of the pultrusion based composite.

- 10 26. A resin system suitable for preparing bulk molding and sheet molding compounds comprising:
- a) about 100 phr of an unsaturated polyester resin;
 - b) about 1 – 5 phr of a crosslinking monomer;
 - c) about 100 – 300 phr of a filler; and
- 15 d) about 0.5 – 5 phr of an alkoxylated phosphate ester of the formula



wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and X is hydrogen or methyl.

- 20 27. The resin system according to claim 26, wherein R is C₈₋₁₆ alkyl, n is 1 to 2, X is hydrogen, and m = 1 - 2.

28. The resin system according to claim 27, further comprising a thickener.

29. The resin system according to claim 28, further comprising a low profile thermoplastic additive.

5

30. The resin system according to claim 29, further comprising a pigment or a dispersion of a pigment.

10

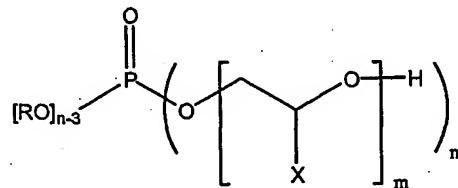
31. The resin system according to claim 30, further comprising a catalyst.

15

32. A bulk molding or sheet molding compound comprising:

a) a resin system comprising

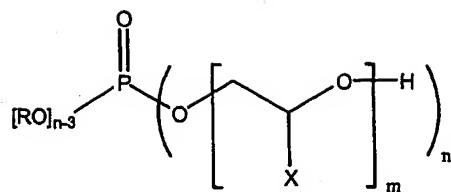
- i) about 100 phr of an unsaturated polyester resin;
- ii) about 1 – 5 phr of a crosslinking monomer;
- iii) about 100 – 300 phr of a filler; and
- iv) about 0.5 – 5 phr of an alkoxylated phosphate ester of the formula



wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and X is hydrogen or methyl; and

20 b) a reinforcement material selected from the group consisting of chopped fiberglass, roving fiberglass, mat fiberglass, carbon fiber or a combination thereof.

33. A bulk molding or sheet molding compound according to claim 32, comprising from about 20 – 70 % by weight of the reinforcement material, based on the total weight of the bulk molding or sheet molding compound.
- 5 34. A method of reducing the relative viscosity of a resin system suitable for preparing plastic components comprising adding to the resin system an effective amount of a viscosity reducing agent, the viscosity reducing agent being an alkoxylated phosphate ester of the formula
-
- 10 wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and X is hydrogen or methyl; and wherein the resin system comprises:
- a) an unsaturated polyester resin;
 - b) a crosslinking monomer; and
 - c) a filler.
- 15 35. The method according to claim 34, wherein R is C₈₋₁₆ alkyl, n is 1 to 2, X is hydrogen, and m = 1 - 2.
36. A method of increasing the secondary adhesion capacity of a plastic component
20 which has been prepared from a resin system, comprising adding to the resin system an effective amount of an adhesion promoter which is an alkoxylated phosphate ester of the formula



wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and X is hydrogen or methyl; and wherein the resin system comprises:

- 5 a) an unsaturated polyester resin;
- b) a crosslinking monomer; and
- c) a filler.

37. The method according to claim 36, wherein R is C₈₋₁₆ alkyl, n is 1 to 2, X is hydrogen, and m = 1 - 2.

10

38. The method according to claim 37, wherein R is C₁₂₋₁₆ alkyl.

15

39. The method according to claim 38, wherein the resin system further comprising a thickener.

15

40. The method according to claim 39, wherein the resin system further comprising a low profile thermoplastic additive.

20

41. The method according to claim 40, wherein the resin system further comprising a pigment or a dispersion of a pigment.

42. The method according to claim 41, wherein the resin system further comprising a

catalyst.

43. The method according to claim 36, wherein the ratio of the adhesion promoter to

(a) is from about 0.20 parts adhesion promoter : 100 parts (a) to about 10 parts

5 adhesion promoter: 100 parts (a).

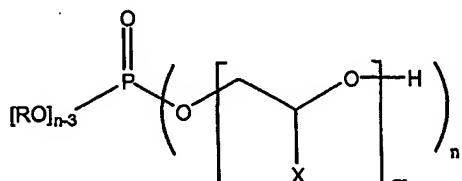
44. The method according to claim 36, wherein the ratio of adhesion promoter to (a)

is from about 0.20 parts adhesion promoter : 100 parts (a) to about 6 parts adhesion

promoter: 100 parts (a).

10

45. A method of increasing the secondary adhesion capacity of a thermosetting composite which has been prepared from a resin system, comprising adding to the resin system an effective amount of an adhesion promoter which is an alkoxylated phosphate ester of the formula



15

wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10;

and X is hydrogen or methyl; and wherein the resin system comprises:

- a) about 100 phr of an unsaturated polyester resin;
- b) about 1 – 5 phr of a crosslinking monomer; and
- c) about 10 – 300 phr of a filler.

20

46. The method according to claim 45, wherein R is C₈₋₁₆ alkyl, n is 1 to 2, X is

hydrogen, and m = 1 - 2.

47. The method according to claim 36, wherein R is C₁₂₋₁₆ alkyl.

48. The method according to claim 47, wherein the resin system further comprising a
5 thickener.

49. The method according to claim 48, wherein the resin system further comprising a
low profile thermoplastic additive.

10 50. The method according to claim 49, wherein the resin system further comprising a
pigment or a dispersion of a pigment.

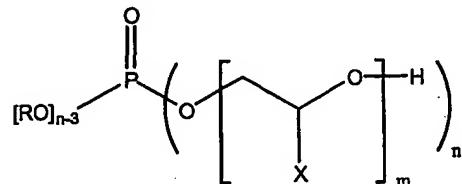
51. The method according to claim 50, wherein the resin system further comprising a
catalyst.

15 52. The method according to claim 51, wherein the resin system further comprises a
reinforcement material selected from the group consisting of chopped fiberglass, roving
fiberglass, or mat fiberglass, carbon fiber or combinations thereof.

20 53. A method according to claim 52, the resin system comprises from about 20 - 70
% by weight of the reinforcement material, based on the total weight of the thermosetting
composite.

54. A method of increasing the secondary adhesion capacity of a pultrusion based

composite which has been prepared from a resin system, comprising adding to the resin system an effective amount of an adhesion promoter which is an alkoxyated phosphate ester of the formula



- 5 wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and X is hydrogen or methyl; and wherein the resin system comprises:
- about 100 phr of an unsaturated polyester resin;
 - about 1 – 5 phr of a crosslinking monomer; and
 - about 20 – 200 phr of a filler.

10 55. The method according to claim 54, wherein R is C₈₋₁₆ alkyl, n is 1 to 2, X is hydrogen, and m = 1 - 2.

56. The method according to claim 55, wherein R is C₁₂₋₁₆ alkyl.

15 57. The method according to claim 56, wherein the resin system further comprising a thickener.

20 58. The method according to claim 57, wherein the resin system further comprising a low profile thermoplastic additive.

59. The method according to claim 58, wherein the resin system further comprising a

pigment or a dispersion of a pigment.

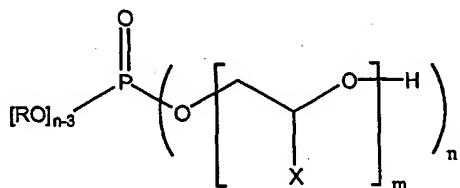
60. The method according to claim 59, wherein the resin system further comprising a catalyst.

5

61. The method according to claim 60, wherein the resin system further comprises a reinforcement material selected from the group consisting of chopped fiberglass, roving fiberglass, or mat fiberglass, carbon fiber or combinations thereof.

10 62. A method according to claim 61, the resin system comprises from about 20 – 70 % by weight of the reinforcement material, based on the total weight of the thermosetting composite.

15 63. A method of increasing the secondary adhesion capacity of a bulk molding and sheet molding compound which has been prepared from a resin system, comprising adding to the resin system an effective amount of an adhesion promoter which is an alkoxylated phosphate ester of the formula



wherein each R is independently alkyl, alkenyl, cycloalkyl, allylic; n is 1 or 2; m = 1 – 10; and X is hydrogen or methyl; and wherein the resin system comprises:

- 20 a) about 100 phr of an unsaturated polyester resin;
 b) about 1 – 5 phr of a crosslinking monomer; and
 c) about 100 – 300 phr of a filler.

64. The method according to claim 63, wherein R is C₈₋₁₆ alkyl, n is 1 to 2, X is hydrogen, and m = 1 - 2.

5 65. The method according to claim 64, wherein R is C₁₂₋₁₆ alkyl.

66. The method according to claim 65, wherein the resin system further comprising a thickener.

10 67. The method according to claim 66, wherein the resin system further comprising a low profile thermoplastic additive.

68. The method according to claim 67, wherein the resin system further comprising a pigment or a dispersion of a pigment.

15 69. The method according to claim 68, wherein the resin system further comprising a catalyst.

70. The method according to claim 69, wherein the resin system further comprises a reinforcement material selected from the group consisting of chopped fiberglass, roving fiberglass, or mat fiberglass, carbon fiber or combinations thereof.

71. A method according to claim 70, the resin system comprises from about 20 - 70 % by weight of the reinforcement material, based on the total weight of the thermosetting

composite.

INTERNATIONAL SEARCH REPORT

| | |
|-----------------|----------------------|
| In | ional Application No |
| PCT/US 01/29686 | |

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08K5/521 C08K7/14 C08K7/06 C08L67/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|--|---|
| X | US 4 282 133 A (FEARING RALPH B ET AL) 4 August 1981 (1981-08-04) cited in the application | 1-3, 7-12, 16, 18-20, 24, 26-28, 32, 34-39, 43, 44 1-71 |
| Y | claims 1-7 | 1-71 |
| Y | US 5 104 983 A (SEETHALER TONI ET AL) 14 April 1992 (1992-04-14) claims 1, 2, 4, 8, 9 | 1-71 |
| Y | EP 0 781 802 A (AJINOMOTO KK) 2 July 1997 (1997-07-02) claims 1, 4, 5 | 1-71 |
| | | -/- |

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority (claims) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the International filing date but later than the priority date claimed

- *T* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the International search

23 November 2001

Date of mailing of the International search report

05/12/2001

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Authorized officer

Rose, E

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/29686

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| Y | US 3 909 484 A (BEAVON ALFRED N) 30 September 1975 (1975-09-30) claims 1,2 ----- | 1-71 |

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/29686

| Patent document cited in search report | | Publication date | | Patent family member(s) | Publication date |
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